The effect of pressure on the rate of the benzidine rearrangement V : 2-chloro-2'-methylhydrazobenzene

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THE EFFECT OF PRESSURE ON THE RATE OF THE BENZIDINE REARRANGEMENT V

2-Chloro-2′-methylhydrazobenzene

BY JIRO OSUGI AND ICHIRO ONISHI

The effect of pressure on the rate of the acid-catalyzed rearrangement of 2-chloro-2′-methylhydrazobenzene in 85 vol% aqueous ethanolic solution was studied under the conditions of 15~30°C and 1~1,500 kg/cm². As a result, it was observed that two different reactions concurred; one was of first order with respect to [HCl] (one-proton mechanism) and the other was of second order (two-proton mechanism), and the former was fairly, while the latter was slightly accelerated by pressure.

Based on the activation parameters obtained, *i.e.* $E^{\ddagger}=22.2$ kcal/mole, $\Delta S^{\ddagger}=-1.6$ e.u., $\Delta V^{\ddagger}=-6.8$ cm³/mole for one-proton mechanism and $E^{\ddagger}=18.0$ kcal/mole, $\Delta S^{\ddagger}=-12.4$ e.u., $\Delta V^{\ddagger}=-3.2$ cm³/mole for two-proton mechanism, the reaction mechanisms and the transition states were discussed. The existence of a linear relationship between the logarithms of the rate constants of the rearrangement and pK_a values of ortho-substituted anilinium ions was suggested, by correcting pK_a for the steric effect of ortho-substituents.

Introduction

The so-called benzidine rearrangement is an acid-catalyzed rearrangement and the rate of the rearrangement of hydrazobenzene is of second order with respect to the acid concentration (two-proton mechanism). But in the cases of 2, 2′-dimethyl-[1a], 2, 2′-dimethoxy-[1b] and 2, 2′-dibromohydrazobenzene[1c], it was observed that the order of reaction in acid fell to one (one-proton mechanism) or that two reactions of first and of second order concurred, depending on the electrostatic character of the substituents. The reactions of one-proton mechanism was found to be always accelerated by pressure irrespective of the substituents.

Considering the negative values of the volume of activation for one-proton mechanism, it was presumed that the transition state of one-proton mechanism was polar, strongly solvated and compact. As the compounds treated previously were all symmetrical, in order to obtain further information about an unsymmetrical compound, the effect of pressure on the rate of the rearrangement of 2-chloro-2′-

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1) a: J. Osugi, M. Sasaki and I. Onishi, *This Journal*, 36, 100 (1966)
b: J. Osugi, M. Sasaki and I. Onishi, *ibid.*, 40, 39 (1970)
c: J. Osugi, M. Sasaki and I. Onishi, *ibid.*, 39, 57 (1969)

methylhydrazobenzene was studied.

Experimentals

Materials

G. R. grade reagents of 99.5 vol% ethanol, of hydrochloric acid and of lithium chloride were used. 2-Chloro-2′-methylazobenzene (A) was synthesized by the condensation of 2-methylaniline and 2-chloronitrosobenzene[2)3)], and a red crystal melting at 84°C was obtained by the recrystallization from ethanol. 2-Chloro-2′-methylhydrazobenzene (B) was prepared by the reduction of (A) with zinc dust and ammonium chloride, and was recrystallized from ethanol, and white crystal melting at 122°C was

Table 1 Molecular extinction coefficients, $\varepsilon \times 10^{-3}$, in 85 vol% aqueous ethanol

Compound	245 mμ	285 mμ	340 mμ
(B)	21.17	4.32	0.02
(P)	4.17	24.60	0.85
(A)	6.76	5.97	15.70

Table 2 Elementary analysis and molecular weight

		C (%)	H (%)	N (%)	Cl (%)	Molecular weight
(B)	Calc.	67.10	5.63	12.04	15.23	232.7
	Found	66.83	5.67	12.09	15.41	231.0
(P)	Calc.	67.10	5.63	12.04	15.23	232.7
	Found	66.99	5.58	12.02	15.35	234.1
(A)	Calc.	67.68	4.81	12.14	15.37	230.7
	Found	67.39	4.94	12.25	15.40	228.2

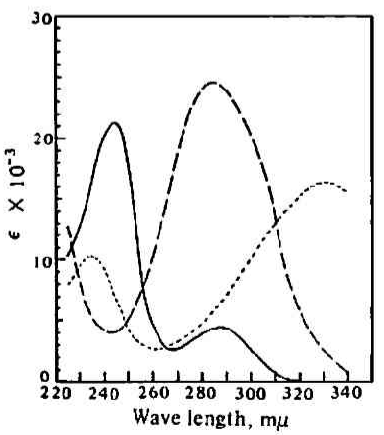

Fig. 1 Molecular extinction coefficients in 85 vol% aqueous ethanolic solution

2) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937)
3) Y. Ogata and Y. Takagi, *J. Am. Chem. Soc.*, **80**, 3591 (1958)

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obtained[4]. 3-Chloro-3′-methylbenzidine (P) was prepared by the rearrangement of (B), was recrystallized from ethanol, and almost colorless crystal melting at 97°C was obtained. Molecular extinction coefficients of (B), (P) and (A) are shown in Table 1 and Fig. 1*).

The results of elementary analysis of (B), (P) and (A), and molecular weights are listed in Table 2.

Procedure

The reaction medium was prepared by mixing 35 vol% aqueous ethanolic solutions of hydrochloric acid and lithium chloride so as to get the fixed concentration, *i.e.* [HCl]=0.05～0.80 mole/*l* for hydrochloric acid and μ=1.00 for ionic strength at high pressure, considering the compressibility of the medium, and the reaction was studied under the conditions of 15～30°C and 1～1,500 kg/cm^2.

The high pressure apparatus used for this work was the same as reported previously[1], but at this time, instead of using a glass syringe, a flexible teflon tube of 6 mm diameter closed with glass rods was used as the reaction vessel under high pressure. After an appropriate time interval, an aliquot of the reaction solution was diluted with an aqueous ethanolic solution of sodium hydroxide, and each component of (B), (P) and (A) in the reaction solution was determined from the absorbances at three wave lengths, 245, 285 and 340 mμ, since it had been already confirmed by thin layer chromatography that no disproportionation reaction occurred.

Results

As the dissolved oxygen was not removed from the reaction solution, both reactions of

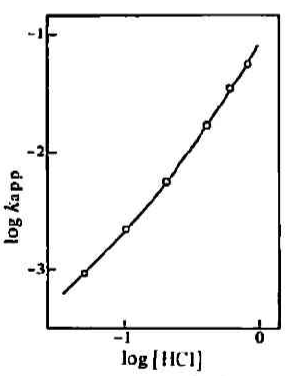


Fig. 2 Dependency of the apparent first order rate constants on the acid concentrations

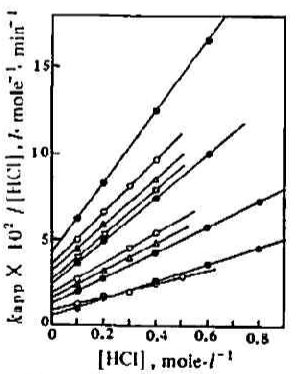


Fig. 3 Dependency of the apparent first order rate constants on the acid concentrations
Pressure (kg/cm^2):
●: 1, □: 500, △: 1,000,
○: 1,500
Temperature (°C):
30, 25, 20, 15 from top to bottom

4) D. V. Banthorpe and A. Cooper, *J. Chem. Soc.*, (B) 1968, 605

*) (B), (P) and (A) are probably new compounds and there are no literatures for melting points.

rearrangement and oxidation concurred. The apparent rate constants of the rearrangement were obtained from the slopes of lines obtained by plotting $\{\Delta[P]/(\Delta[P]+\Delta[A])\}\log([B]_0/[B])$ *versus* time, where $\Delta[P]$ and $\Delta[A]$ indicate the increases of (P) and (A) at a fixed reaction time and $[B]_0$ indicates the initial concentration of (B).

Fig. 2 illustrates the relationship between the apparent rate constants and the acid concentrations in which the slope of the curve continuously increases with increasing acidity. Therefore, it is obvious that two reactions occur, *i.e.* one is of first order with respect to the acid concentration (one-proton mechanism) and the other is of second order (two-proton mechanism).

$$k_{app}=k_1[HCl]+k_2[HCl]^2,$$

$$\frac{k_{app}}{[HCl]}=k_1+k_2[HCl],$$

$$B \underset{}{\overset{H^+ \quad K_1}{\rightleftharpoons}} BH^+ \overset{H^+ \quad K_2 \text{ or } k'}{\rightleftharpoons} BH_2^{++}$$

$$BH^+ \xrightarrow{k_1^*} P \qquad BH_2^{++} \underset{k'_{-1}}{\overset{}{\rightleftharpoons}} \xrightarrow{k_2^*} P$$

where k' is the rate constant of the rate-determining step when the second protonation is slow.

The rate constants of one-proton mechanism k_1 and of two-proton mechanism k_2 summarized in Table 3 were obtained from Fig. 3 in which $k_{app}/[HCl]$ is plotted against [HCl]. Figs. 4 and 5 illustrate the dependencies of the rate constants on temperature and pressure. The activation parameters are summarized in Table 4.

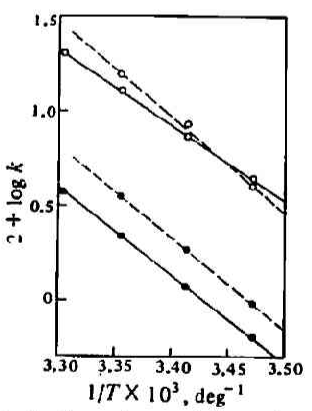


Fig. 4 Dependency of the rate constants of the rearrangement on temperature
●: one-proton,
○: two-proton,
—— 1 kg/cm²,
---- 1,500 kg/cm²

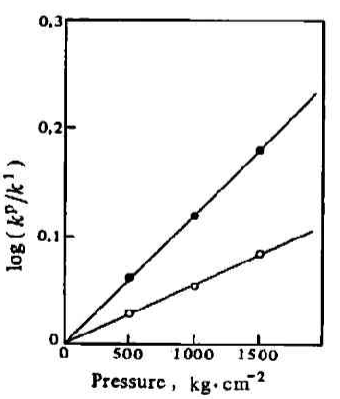


Fig. 5 Dependency of the rate constants of the rearrangement on pressure
●: one-proton,
○: two-proton

Table 3 The rate constants of the rearrangement ($\mu=1.00$)

Temp. (°C)	Pressure (kg/cm²)	$k_1\times10^2$ ($l\cdot mole^{-1}\cdot min^{-1}$)	$k_2\times10^2$ ($l^2\cdot mole^{-2}\cdot min^{-1}$)
15	1	0.65	4.36
	1,500	0.95	4.10
20	1	1.26	7.50
	1,000	1.64	8.02
	1,500	1.87	8.80
25	1	2.35	12.7
	500	2.71	13.6
	1,000	3.10	14.4
	1,500	3.55	15.5
30	1	4.30	20.4

Table 4 The activation parameters for the rearrangement

	$\Delta V^{\ddagger}$ (cm³/mole)	Pressure (kg/cm²)	$E^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
k_1 (one-proton)	−6.8	1	22.2	−1.6
		1,500	22.6	0.6
k_2 (two-proton)	−3.2	1	18.0	−12.4
		1,500	22.4	2.9

One-proton mechanism : $\left(\frac{\Delta\Delta V}{\Delta T}\right)=-0.08$, $\left(\frac{\Delta\Delta S}{\Delta P}\right)=0.06$

Two-proton mechanism : $\left(\frac{\Delta\Delta V}{\Delta T}\right)=-0.42$, $\left(\frac{\Delta\Delta S}{\Delta P}\right)=0.42$

Discussions

On the one-proton mechanism, the value of −6.8 cm³/mole of the apparent volume of activation is similar to the values of other one-proton mechanism, *i.e.* −2.5 cm³/mole for 2, 2′-dimethyl-[1a], −10.7 cm³/mole for 2, 2′-dibromo-[1c] and −12 cm³/mole for 2, 2′-dimethoxyhydrazobenzene[1b]. Since the volume changes of pre-equilibrium of the protonation are presumed to be about −5 cm³/mole[5], not only Ingold's postulation, that is the so-called polar transition state theory[6], is supported, but also it can be assumed that these transition states are so compact and strongly solvated, and that the volume increases due to the fission of NH_2^+: NH after the protonation can be sufficiently overcome.

For the two-proton mechanism, the apparent volumes of activation obtained, *i.e.* −3.2 cm³/mole in this study, −7.2 cm³/mole for 2, 2′-dimethyl-[1a], −0.4 cm³/mole for 2, 2′-dibromohydrazobenzene[1c] and 1.5 cm³/mole for hydrazobenzene[7], are either slightly negative or slightly positive. Since the

5) E. Whalley, *Trans. Faraday Soc.*, 55, 798 (1959)
6) D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1964, 2864
7) J. Osugi and T. Hitouji. *This Journal*, 34, 88 (1964)

volume changes of the pre-equilibrium of the first and second protonation are presumed to be both negative, it is reasonable that the apparent volumes of activation of the two-proton mechanism are either slightly negative or slightly positive, because the volume decrease of the protonation ($\Delta V_{K_1}+\Delta V_{K_2}$) is comparable to the volume increase of the fission of $\overset{+}{N}H_2:NH_2^+$ ($\Delta V_{k_2}^*$). At all events, the transition state of the two-proton mechanism is considered to be somewhat less polar.

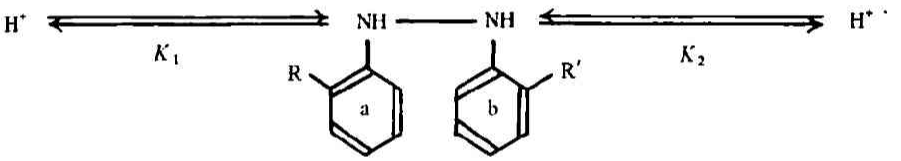
As the reactions of ortho-substituted compounds do not obey the Hammett law, the relationship between the rates of the rearrangements and the pK_a values of ortho-substituted anilinium ions which correspond to the conjugate acids of aniline moieties of 2, 2′-disubstituted-hydrazobenzene, is considered.

The apparent rate constants of one-proton mechanism k_1 ($l\cdot mole^{-1}\cdot min^{-1}$) and that of two-proton mechanism k_2 ($l^2\cdot mole^{-2}\cdot min^{-1}$) are indicated as follows.

$$k_1=k_1^*K_1\,, \tag{1}$$

$$k_2=k_2^*K_1K_2 \quad \text{or} \quad k_2=k'K_1\,, \tag{2}$$

where K_1 and K_2 indicate the equilibrium constants of the first protonation on a-ring and of the second protonation on b-ring, respectively.



Although it is presumed that pK_a value of diprotonated cation in which two vicinal nitrogen atoms exist is probably 9 or 10, smaller than that of monoprotonated cation[8)9)], the relationship between pK_a of monoprotonated hydrazo-compound and that of free anilinium ion is not obvious. Provided that the equilibrium constants of the protonation for 2, 2′-disubstituted-hydrazobenzene, K_1 and K_2, are proportional to that for ortho-substituted-aniline, K_1 and K_2, equations (1) and (2) can be expressed as follows,

$$k_1=k_1^*\rho K_1\,, \tag{3}$$

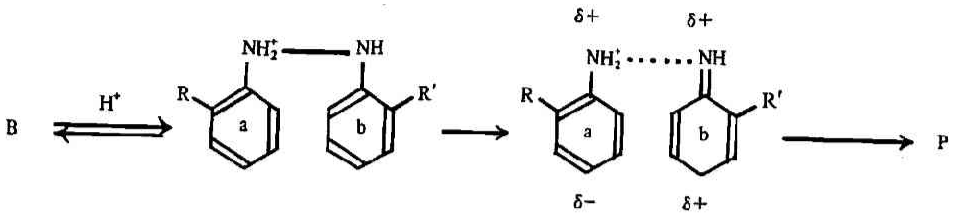
$$k_2=k_2^*\rho' K_1K_2\,, \tag{4}$$

$$\text{or} \quad k_2=k'\rho'' K_1\,, \tag{4'}$$

where ρ, ρ' and ρ'' are proportional constants.

Then in the case of the one-proton mechanism, after the first protonation on a-ring, the electrons which exist between two nitrogen atoms, $\overset{+}{N}H_2:NH$, move from b- to a-ring and the heterolytic fission is facilitated as postulated by Ingold. The rate constant of the rate-determining step k_1^* is probably proportional to the donative character of electrons from b- to a-ring, or to the electron density of NH,

8) J. Clark and D. D. Perrin, *Quart. Rev.*, **18**, 295 (1964)
9) V. Sterba and M. Vecera. *Collect. Czech. Chem. Commun.*, **31**, 3486 (1966)



or to the basicity of b-ring, and it is probably proportional to the basicity of corresponding aniline (b). Therefore, equation (3) becomes as follows,

$$k_1=\rho\alpha K_1K_2\,. \tag{5}$$

where $k_1{}^*=\alpha K_2$, and α is a proportional constant.

For the two-proton mechanism, if the second protonation is in pre-equilibrium and the following fission has no correlation with the basicity of the ring, then equation (4) is left as it is. If the second protonation is in the rate-determining step, the ease of the protonation probably depends on the basicity of b-ring and k' is proportional to K_2, and equation (4') can be rewritten,

$$k_2=\rho'\beta K_1K_2\,, \tag{6}$$

where β is a proportional constant.

Therefore, in either case, the apparent rate constants of the rearrangement, k_1 and k_2, are given as follows,

$$\left.\begin{aligned} &k_1=\rho\alpha K_1K_2\,,\\ &k_2=\rho' k_2{}^*K_1K_2 \quad\text{or}\quad k_2=\rho''\beta K_1K_2\,. \end{aligned}\right\} \tag{7}$$

And further, these rate constants, k_1 and k_2, are indicated by pK_a of anilinium ion as follows,

$$\left.\begin{aligned} &\log k_1=\log(\rho\alpha)+pK_{a1}+pK_{a2}\,,\\ &\log k_2=\log(\rho'k_2{}^*)+pK_{a1}+pK_{a2}\,,\\ \text{or}\quad &\log k_2=\log(\rho''\beta)+pK_{a1}+pK_{a2}\,. \end{aligned}\right\} \tag{8}$$

The pK_a values of conjugate anilinium ions of ortho-substituted aniline in 85 vol% aqueous ethanolic solution were obtained by referring to the deduction by J. Clark and D. D. Perrin[9], and to the values obtained by Grunwald[10] and Ingold[11] as summarized in Table 5. And as a trial, as shown in Fig. 6, the logarithms of the rate constants, k_1($l\cdot$mole$^{-1}\cdot$min^{-1}) and k_2($l^2\cdot$mole$^{-2}\cdot$min^{-1}), of the rearrangement of 2-chloro-2'-methylhydrazobenzene ($k_1=2.35\times10^{-2}$, $k_2=12.7\times10^{-2}$) and that of other hydrazocompounds reported previously, *i.e.* 2, 2'-dimethylhydrazobenzene ($k_1=0.573$, $k_2=3.0$)[1a], 2, 2'-di-

10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions" p. 228, p. 268, John Wiley and Sons, Inc., New York and London (1963)

11) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", p. 741, Cornell University Press, Ithaca, New York (1953)

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bromohydrazobenzene ($k_1=1.6\times10^{-4}$, $k_2=2.3\times10^{-4}$)[1c], 2, 2′-dimethoxyhydrazobenzene ($k_1=270$)[1b] and hydrazobenzene ($k_2=3.57$)[7], were plotted against the values of ($pK_{a1}+pK_{a2}$). Although the ethanol content of the reaction medium of 2, 2′-dimethylhydrazobenzene and hydrazobenzene are different from those cases of other compounds, a straight line of slope of 1.04 and the correlation coefficient of 0.99 were obtained for one-proton mechanism by the least square method. Therefore, it is clear that $\log k_1$ is closely correlated with ($pK_{a1}+pK_{a2}$).

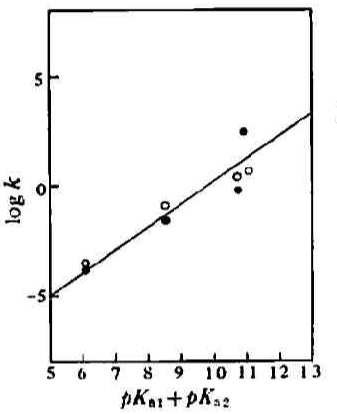


Fig. 6 Trial plot of $\log k$ against ($pK_{a1}+pK_{a2}$)
●: one-proton,
○: two-proton

As shown in Fig. 6, in the case of 2, 2′-dimethoxyhydrazobenzene, a large divergence from a straight line is observed and it is probably due to the steric effect of the substituents which is different from those of the other substituents. The electron donation which causes the fission does not result from the protonated a-ring $RC_6H_4NH_2^+$-, but from the electro-neutral un-protonated b-ring, $R'C_6H_4NH$-. The basicity or pK_a is not reasonable for this point because the effects of substituent R′ on b-ring would appear synthetically including the induced resonance effect and the steric effect for H^+ addition. It is necessary to estimate the electron density of NH of electro-neutral 2′-methoxyaniline ring (b-ring), by reducing the steric effect which hinders the approach of H^+ to b-ring.

Taft's steric factor of the ortho-substituent is indicated by E_s, and if the electron density of NH of electro-neutral 2′-methoxyaniline ring (b-ring) is expressed by the value of ($pK_{a2}+\gamma E_s$) obtained by deducting the steric effect from pK_{a2}, the rate constant of the rearrangement of one-proton mechanism becomes as follows.

Table 5 pK_a values of the ortho-substituted anilinium ions (25°C, 85 vol% aqueous ethanolic solution) and the steric factors E_s of the ortho-substituents

Substituents	pK_a	E_s [10]
2	5.55	
2 OCH_3	5.44	+0.99
2 CH_3	5.35	0.00
2 F	3.52	+0.49
2 Cl	3.15	+0.18
2 Br	3.06	0.00
2 I	2.62	−0.20

$$\log k_1 = \log(\rho\alpha) + (pK_{a1} + pK_{a2} + \gamma E_s), \qquad (9)$$

where γ is a proportional constant.

Table 6 The scales of abscissa when $\log k_1$ and $\log k_2$ are plotted

Substituents	One-proton $pK_{a1} - pK_{a2} + \gamma E_s$	Two-proton $pK_{a1} + pK_{a2}$
2 OCH_3, 2′ OCH_3	12.2	10.9
2 CH_3, 2′ CH_3	10.7	10.7
2 Cl, 2′ CH_3	8.5	8.5
2 Br, 2′ Br	6.1	6.1

Using the values, $\log(\rho\alpha) = -10.0$ and $\gamma = 1.51$, which were obtained from the assumption that a straight line of slope of 1.00 is obtained for the one-proton mechanism of 2, 2′-dibromo- and 2, 2′-dimethoxyhydrazobenzene, the data were plotted again in Fig. 7.

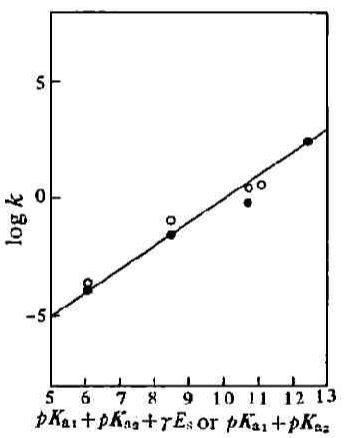


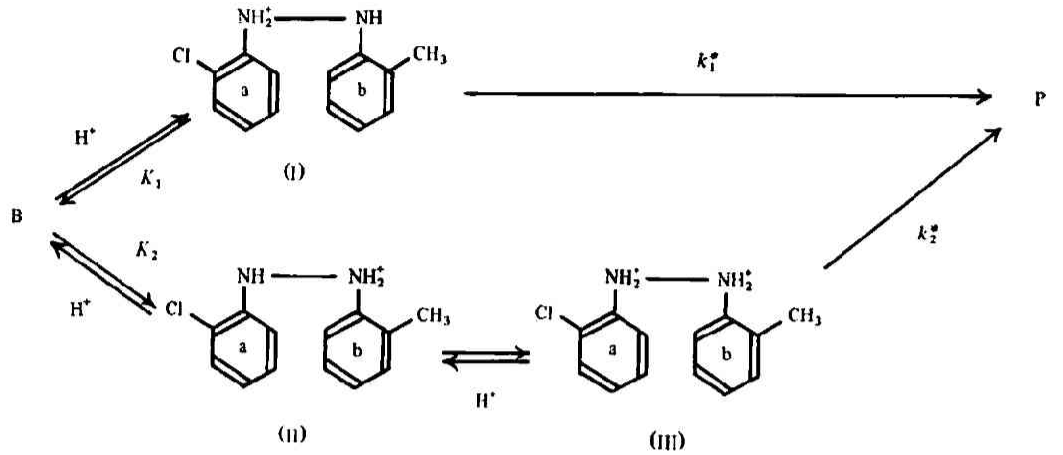
Fig. 7 The linear free energy relationship
●: one-proton,
○: two-proton

Not only the data for 2, 2′-dibromo- and 2, 2′-dimethoxyhydrazobenzene, but also the data for 2-chloro-2′-methylhydrazobenzene show the straight line and the good correlation is obtained. In the latter case, it is presumed that the ortho-substituent of b-ring is methyl radical and not chlorine, because otherwise the linearity would be changed to the worse. Therefore, whether the rearrangement reaction is the one-proton mechanism or not, is determined by considering which ring of the two, a or b, is protonated at first step. That is, it is concluded that the reaction is the one-proton mechanism when the first protonation occurs in less basic 2-chloroaniline ring (a-ring).

Considering the difference between pK_a of 2-methylanilinium ion (5.35) and that of 2-chloroanilinium ion (3.15), the concentration of mono-protonated cation (II), protonated to methyl-substituted b-ring, is about 100 times as large as that of mono-protonated cation (I), protonated to chlorine-substituted a-ring.

If the pK_a value of diprotonated cation (III) in which two vicinal nitrogen atoms (NH_2^+ and NH_2^+) exist is presumed to be 9 or 10, smaller[8)9)] than that of mono-protonated cation (I), as described above, the concentration of mono-protonated cation (I) is $10^7 \sim 10^8$ times as large as that of diprotonated cation

(III). Therefore, it is considered that the rate constant of the rate-determining step of the two-proton mechanism k_2^* is $10^8 \sim 10^9$ times as large as that of the one-proton mechanism k_1^*.



Although it is difficult to reach the conclusion on the two-proton mechanism, because of the scantiness of the data, if the linear relationship is assumed to be established between $\log k_2$ and the value of $(pK_{a1}+pK_{a2})$, the slope of the line shoud be somewhat large. Therefore, if the first and the second protonations are in pre-equilibrium, it is considered that the electron-donative effect of the substituents influences more or less the rate constant of the rate-determining step. These considerations would make further studies of this problem necessary.

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